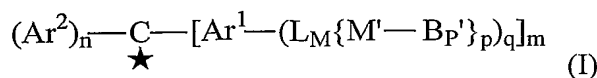


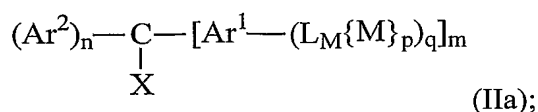
## CLAIMS

1. A method of forming an ion of formula (I):

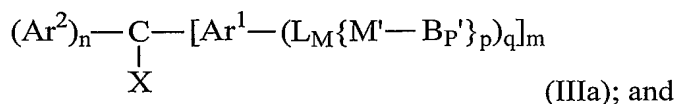


comprising the steps of:

- 5 (i) reacting a compound of the formula (IIa):



with a biopolymer,  $\text{B}_P$ , having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIa):



- 10 (ii) cleaving the C—X bond between X and the  $\alpha$ -carbon atom of the derivative of formula (IIIa) to form the ion of formula (I);

where:

C $\star$  is a carbon atom bearing a single positive charge or a single negative charge;

X is a group capable of being cleaved from the  $\alpha$ -carbon atom to form an ion of formula (I);

- 15 M is independently a group capable of reacting with  $\text{B}_P$  to form the covalent linkage;

$\text{B}_P'$  is independently the biopolymer residue of  $\text{B}_P$  produced on formation of the covalent linkage;

M' is independently the residue of M produced on formation of the covalent linkage;

$\text{Ar}^1$  is independently an aromatic group or an aromatic group substituted with one or more A;

- 20  $\text{Ar}^2$  is independently an aromatic group or an aromatic group substituted with one or more A;

optionally wherein (a) two or three of the groups  $\text{Ar}^1$  and  $\text{Ar}^2$  are linked together by one or more  $\text{L}^5$ , where  $\text{L}^5$  is independently a single bond or a linker atom or group; and/or (b) two or three of the groups  $\text{Ar}^1$  and  $\text{Ar}^2$  together form an aromatic group or an aromatic group substituted with one or more A;

- 25 A is independently a substituent;

$\text{L}_M$  is independently a single bond or a linker atom or group;

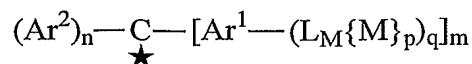
$n = 0, 1$  or  $2$  and  $m = 1, 2$ , or  $3$ , provided the sum of  $n+m = 3$ ;

p independently = 1 or more; and

q independently = 1 or more.

2. A method of forming an ion of formula (I), comprising the steps of:

(i) reacting a compound of the formula (IIb):

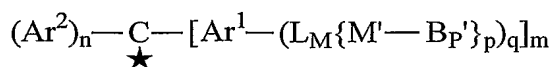


5

X★

(IIb);

with a biopolymer, B<sub>P</sub>, having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIb):



X★

(IIIb); and

dissociating X★ from the derivative of formula (IIIb), to form the ion of formula (I);

10 where:

X★ is a counter-ion to C★;

and C★, M, B<sub>P</sub>', M', Ar<sup>1</sup>, Ar<sup>2</sup>, L<sub>M</sub>, n, m, p and q are as defined in claim 1.

3. A biopolymer derivative of the formula (IIIa).

15

4. A biopolymer derivative of the formula (IIIb).

5. An ion of formula (I).

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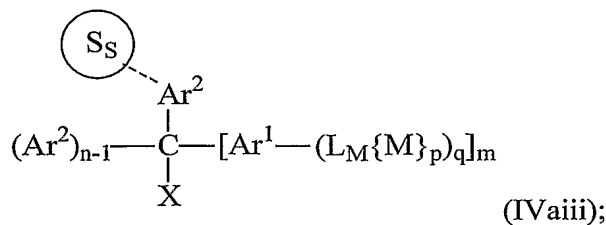
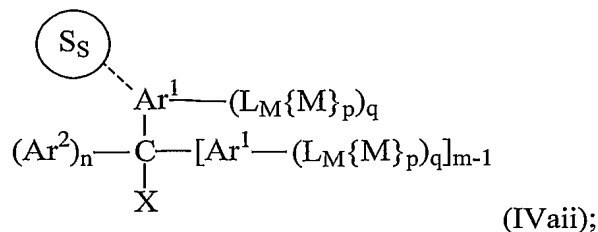
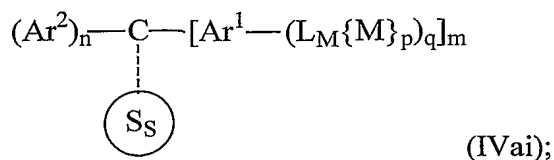
6. A compound of the formula (IIa).

7. A compound of the formula (IIb).

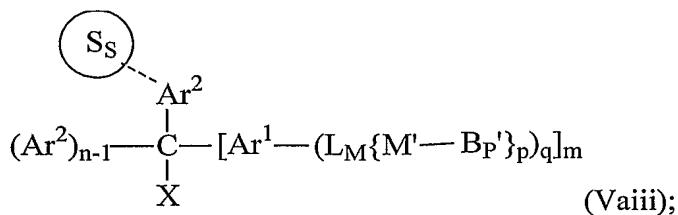
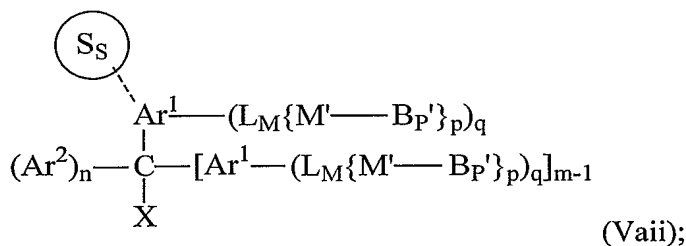
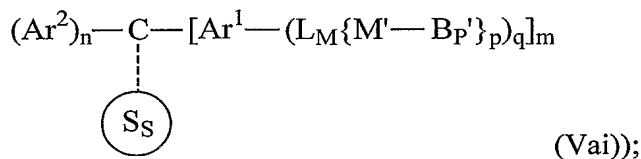
8. A method of forming an ion of formula (I) comprising the steps of:

25

(i) reacting a solid support of formula (IVai), (IVaii), or (IVaiii):



with a biopolymer, B<sub>P</sub>, having at least one group capable of reacting with M to form a covalent  
 5 linkage, to provide a modified solid support of the formula (Vai), (Vaii), or (Vaiii), respectively:



and either:

- 10 (ia) for modified solid supports of formula (Vai) cleaving the C-S<sub>S</sub> bond between the α-carbon atom of the modified solid support of formula (Vai) and the solid support S<sub>S</sub> to form the ion of formula (I);

(iib) for modified solid supports of formula (Vaii), either simultaneously or sequentially, cleaving the C-X bond between X and the  $\alpha$ -carbon atom and cleaving the SS- -Ar1 bond between the solid support and the Ar1 group to form the ion of formula (I); or

(iic) for modified solid supports of formula (Vaiii), either simultaneously or sequentially, cleaving the C-X bond between X and the  $\alpha$ -carbon atom and cleaving the SS- -Ar2 bond between the solid support and the Ar2 group to form the ion of formula (I);

where:

X, Ar<sup>1</sup>, Ar<sup>2</sup>, B<sub>P</sub>', L<sub>M</sub>, M, M', n, m, p and q are as defined in claim 1;

S<sub>S</sub> is a solid support;

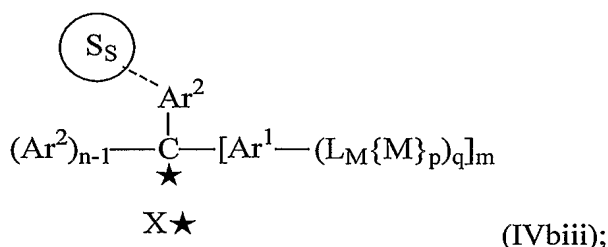
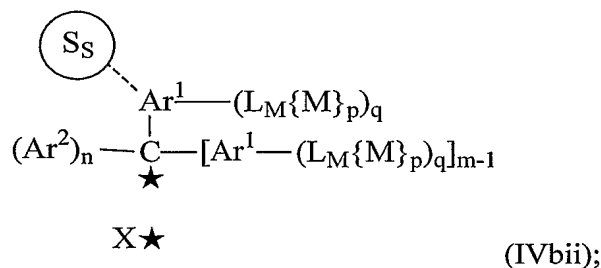
10 C---S<sub>S</sub> comprises a cleavable bond between C and S<sub>S</sub>;

S<sub>S</sub>---Ar<sup>1</sup> comprises a cleavable bond between Ar<sup>1</sup> and S<sub>S</sub>; and

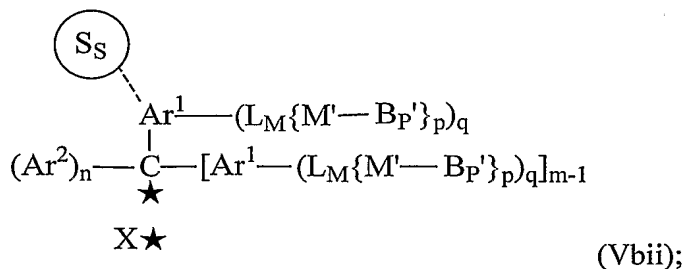
S<sub>S</sub>---Ar<sup>2</sup> comprises a cleavable bond between Ar<sup>2</sup> and S<sub>S</sub>.

9. A method of forming an ion of formula (I) comprising the steps of:

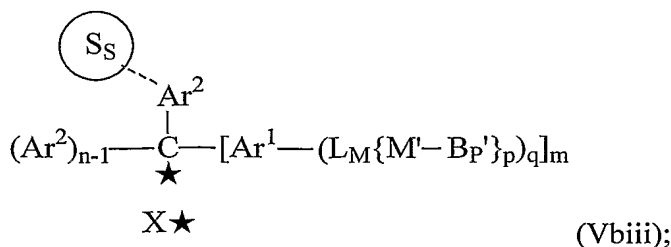
15 (i) reacting a solid support of formula (IVbii) or (IVbiii):



with a biopolymer, B<sub>P</sub>, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vbii) or (Vbiii), respectively:



20



and either:

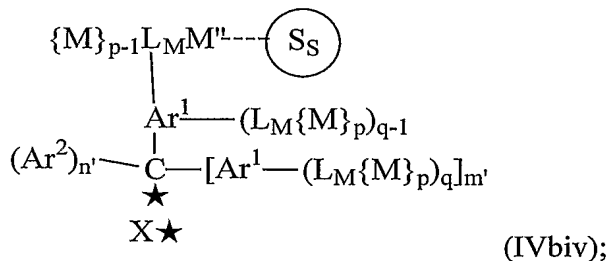
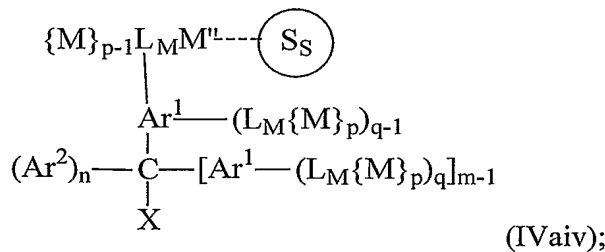
(iia) for modified solid supports of formula (Vbii), either simultaneously or sequentially, dissociating  $\text{X}\star$  from the derivative of formula (Vbii) and cleaving the  $\text{S}_\text{S} - \text{Ar}^1$  bond between the solid support and the  $\text{Ar}^1$  group to form an ion of formula (I); or

(iib) for modified solid supports of formula (Vbiii), either simultaneously or sequentially, dissociating  $\text{X}\star$  from the derivative of formula (Vbiii) and cleaving the  $\text{S}_\text{S} - \text{Ar}^2$  bond between the solid support and the  $\text{Ar}^2$  group to form an ion of formula (I);

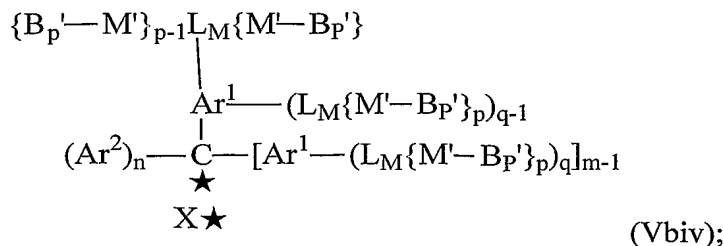
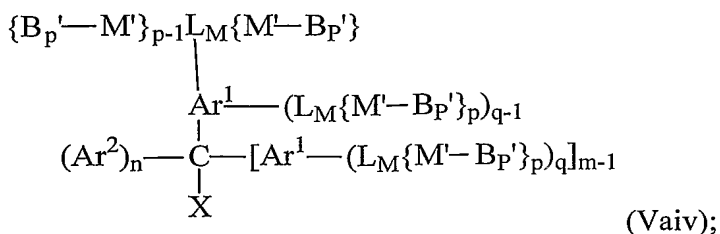
where:  $\text{X}\star$ ,  $\text{Ar}^1$ ,  $\text{Ar}^2$ ,  $\text{B}_\text{P}'$ ,  $\text{L}_\text{M}$ ,  $\text{M}$ ,  $\text{M}'$ ,  $n$ ,  $m$ ,  $p$ ,  $q$ ,  $\text{S}_\text{S}$ ,  $\text{C} - \text{S}_\text{S}$ ,  $\text{S}_\text{S} - \text{Ar}^1$  and  $\text{S}_\text{S} - \text{Ar}^2$  are as defined in claim 8.

10. A method of forming an ion of formula (I) comprising the steps of:

(i) reacting a solid support of formula (IVaiv) or (IVbiv):



with a biopolymer,  $\text{B}_\text{P}$ , having at least one group capable of reacting with  $\text{M}$  to form a covalent linkage, to provide a modified solid support of the formula (Vaiv) or (Vbiv), respectively:



and either:

(iia) for modified solid supports of formula (Vaiv), cleaving the C-X bond  
5 between X and the  $\alpha$ -carbon atom to form the ion of formula (I); or

(iib) for modified solid supports of formula (Vbiv), dissociating  $X\star$  from the  
derivative of formula (Vbiv) to form the ion of formula (I);

where:

X,  $X\star$ ,  $Ar^1$ ,  $Ar^2$ ,  $B_{p'}$ ,  $L_M$ , M,  $M'$ , p, q, n, m, and  $S_S$  are as defined in claims 8 and 9;

10  $M''-S_S$  comprises a bond between  $M''$  and  $S_S$ ; and

$M''$  is the same as M except that  $S_S$  is bound to a portion of M which does not form part of  
M'.

11. A solid support of the formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv).

15

12. A modified solid support of the formula (Vai), (Vaii), (Vaiii), (Vaiv), (Vbii), (Vbiii) or  
(Vbiv).

13. A method of any of claims 8-10 or a product of claim 11 or 12 wherein the biopolymer is a  
20 synthetic biopolymer.

14. A method or product of claim 13 wherein the synthetic biopolymer is an oligonucleotide, a  
peptide or a carbohydrate.

15. A method for analysing a biopolymer, B<sub>P</sub>, comprising the steps of:

(i) reacting the biopolymer B<sub>P</sub> with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv);

(ii) providing an ion of formula (I); and

5 (iii) analysing the ion of formula (I) by mass spectrometry.

16. In a method for analysing a biopolymer, B<sub>P</sub>, the improvement consisting of: (i) reacting a biopolymer, B<sub>P</sub> with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv); (ii) providing an ion of formula (I); and (iii)

10 analysing the ion by mass spectrometry.

17. A method of claim 15 or claim 16 wherein the analysis by mass spectrometry is carried out in a spectrometer which is suitable for MALDI-TOF spectrometry.

15 18. A method of any of claims 1, 2, 8-10 or 13-17 or a product of any of claims 3-7, 11 or 12, wherein C★ bears a single positive charge, such that the ions of formulae (I), (IIb) and (IIIb) have the structures:

Formula (I)	$(Ar^2)_n - \overset{\oplus}{C} - [Ar^1 - (L_M - \{M' - B_{P'}\}_p)_q]_m$
Formula (IIb)	$(Ar^2)_n - \overset{\oplus}{C} - [Ar^1 - (L_M - \{M\}_p)_q]_m$ $X^\ominus$
Formula (IIIb)	$(Ar^2)_n - \overset{\oplus}{C} - [Ar^1 - (L_M - \{M' - B_{P'}\}_p)_q]_m$ $X^\ominus$

19. A method of any of claims 1, 2, 8-10 or 13-18 or a product of any of claims 3-7, 11, 12 or 18  
20 wherein n = 2 and m = 1.

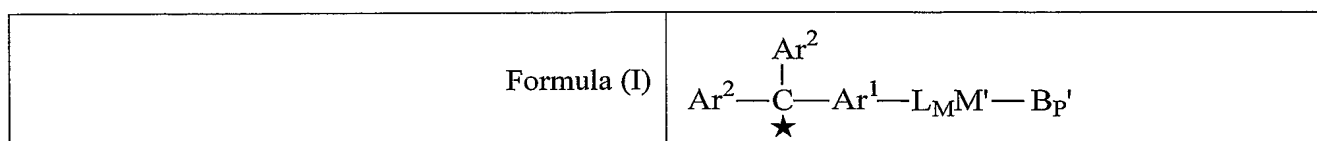
20. A method of any of claims 1, 2, 8-10 or 13-19 or a product of any of claims 3-7, 11, 12, 18 or 19 wherein p = 1, 2 or 3.

25 21. A method of any of claims 1, 2, 8-10 or 13-20 or a product of any of claims 3-7, 11, 12 or 18-20 wherein p = 1.

22. A method of any of claims 1, 2, 8-10 or 13-21 or a product of any of claims 3-7, 11, 12 or 18-21 wherein  $q = 1, 2$  or  $3$ .

5 23. A method of any of claims 1, 2, 8-10 or 13-22 or a product of any of claims 3-7, 11, 12 or 18-22 wherein  $q = 1$ .

24. A method of any of claims 1, 2, 8-10 or 13-23 or a product of any of claims 3-7, 11, 12 or 18-23 wherein  $n = 2$ ,  $m = 1$ ,  $p = 1$  and  $q = 1$ , such that the ion of formula (I) has the structure:



10

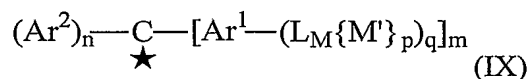
25. A method of any of claims 1, 2, 8-10 or 13-24 or a product of any of claims 3-7, 11, 12 or 18-24 wherein the biopolymer is a polymer found in biological samples.

15 26. A method or product of claim 25 wherein the biopolymer is a polypeptide, polysaccharide, or polynucleotide.

27. A method or product of claim 26 wherein the biopolymer is a polypeptide.

20 28. A method or product of any of claims 25-27 wherein the biopolymer does not readily form a molecular ion on illumination of laser light at 340 nm.

29. A method of any of claims 1, 2, 8-10 or 13-28 or a product of any of claims 3-7, 11, 12 or 18-28 wherein the ratio  $m(\text{B}_P') / m(\text{IX})$  is more than 2, where  $m(\text{IX})$  is the mass of the fragment (IX)



25 of the cation of formula (I) and  $m(\text{B}_P')$  is the mass of the biopolymer residue  $\text{B}_P'$ .

30. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein  $M$  is:  $-\text{NR}_2$ ;  $-\text{SR}$ ;  $-\text{OR}$ ;  $-\text{B}(\text{R})\text{Y}$ ;  $-\text{BY}_2$ ;  $-\text{C}(\text{R})_2\text{Y}$ ;  $-\text{C}(\text{R})\text{Y}_2$ ;  $-\text{CY}_3$ ;  $-\text{C}(=\text{Z})\text{Y}$ ;



-Z-C(=Z)Y; -C(=Z)R; -C(R)(OH)OR; -C(R)(OR)<sub>2</sub>; -S(=O)Y; -Z-S(=O)Y; -S(=O)<sub>2</sub>Y; -Z-S(=O)<sub>2</sub>Y; -S(=O)<sub>3</sub>Y; -Z-S(=O)<sub>3</sub>Y; -P(=Z)(ZR)Y; -P(=Z)Y<sub>2</sub>; -Z-P(=Z)(ZR)Y; -Z-P(=Z)Y<sub>2</sub>; -P(=Z)(R)Y; -Z-P(=Z)(R)Y; or -N=C(=Z), where Y is independently a leaving group, Z is independently O, S or N(R) and R is independently H, C<sub>1-8</sub>hydrocarbyl or C<sub>1-8</sub>hydrocarbyl substituted with one or more A.

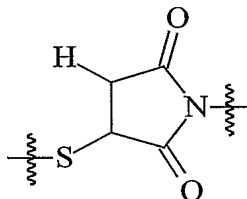
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31. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: -N(R)-; -S-; -O-; -B(Y)-; -C(R)(Y)-; -CY<sub>2</sub>-; -C(=O)-; -C(OH)(OR)-; or -C(OR)<sub>2</sub>-, where Y is independently a leaving group and R is independently H, C<sub>1-8</sub>hydrocarbyl or C<sub>1-8</sub>hydrocarbyl substituted with one or more A.

10

32. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is:  $\text{---}\overset{\text{Y}}{\underset{|}{\text{C}}}\text{---}$ , where Y is a leaving group.

33. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein the covalent linkage is selected from those produced through the reaction of one the



following groups: -CO-NH-; biotin-(strept)avidin; ; or -NH-CS-NH-.

34. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L<sub>M</sub> is O or S.

20

35. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L<sub>M</sub> is -E<sup>M</sup>-, -(D<sup>M</sup>)<sub>t</sub>-, -(E<sup>M</sup>-D<sup>M</sup>)<sub>t</sub>-, -(D<sup>M</sup>-E<sup>M</sup>)<sub>t</sub>-, -E<sup>M</sup>-(D<sup>M</sup>-E<sup>M</sup>)<sub>t</sub>- or -D<sup>M</sup>-(E<sup>M</sup>-D<sup>M</sup>)<sub>t</sub>- (in the orientation Ar<sup>1</sup>-(L<sub>M</sub>{M}<sub>p</sub>)<sub>q</sub> or Ar<sup>1</sup>-(L<sub>M</sub>{M'}<sub>p</sub>)<sub>q</sub>, as appropriate),

where:

25 a sufficient number of linking covalent bonds, in addition to the covalent bonds at the chain termini shown, are provided on groups E<sup>M</sup> and D<sup>M</sup> for linking the p instances of M (or M') groups;

D<sup>M</sup> is independently C<sub>1-8</sub>hydrocarbylene or C<sub>1-8</sub>hydrocarbylene substituted with one or more A;

E<sup>M</sup> (in the orientation Ar<sup>1</sup>-(L<sub>M</sub>{M}<sub>p</sub>)<sub>q</sub> or Ar<sup>1</sup>-(L<sub>M</sub>{M'}<sub>p</sub>)<sub>q</sub>, as appropriate) is independently -Z<sup>M</sup>-, -C(=Z<sup>M</sup>)-, -Z<sup>M</sup>C(=Z<sup>M</sup>)-, -C(=Z<sup>M</sup>)Z<sup>M</sup>-, -Z<sup>M</sup>C(=Z<sup>M</sup>)Z<sup>M</sup>-, -S(=O)-, -Z<sup>M</sup>S(=O)-, -S(=O)Z<sup>M</sup>-,

$-Z^M S(=O)Z^M-$ ,  $-S(=O)_2-$ ,  $-Z^M S(=O)_2-$ ,  $-S(=O)_2 Z^M-$ ,  $-Z^M S(=O)_2 Z^M-$ , where  $Z^M$  is independently O, S or N( $R^M$ ) and where  $R^M$  is independently H,  $C_{1-8}$ hydrocarbyl (e.g.  $C_{1-8}$ alkyl) or  $C_{1-8}$ hydrocarbyl substituted with one or more A; and

$t = 1$  or more.

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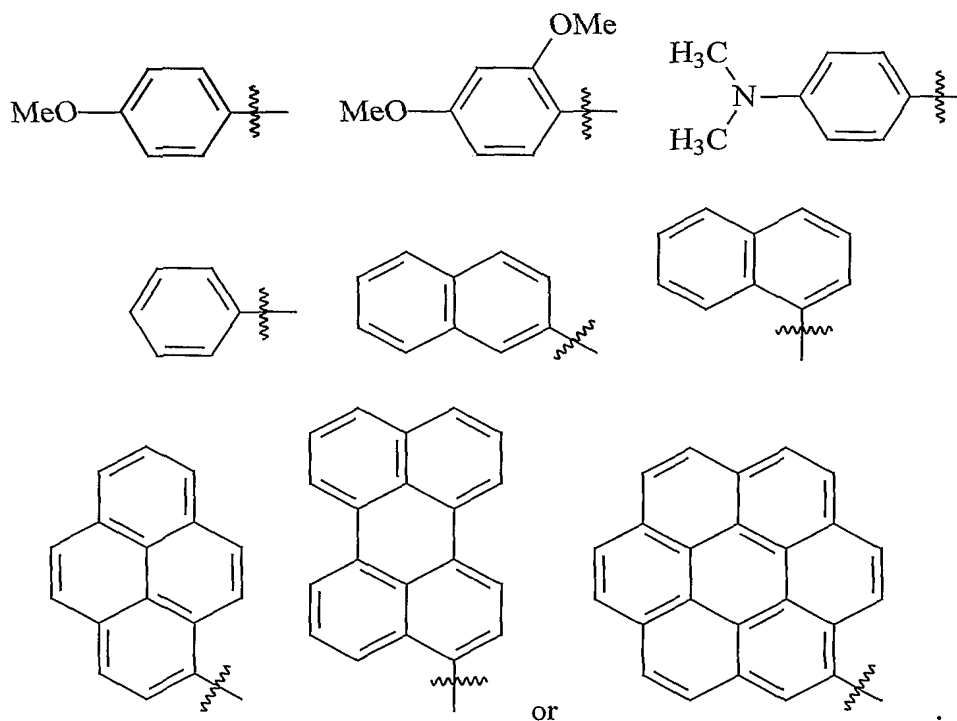
36. A method of any of claims 1, 8, 10 or 13-35 or a product of any of claims 3, 6, 11, 12 or 18-35 wherein the group X is halogen, hydroxy,  $C_{1-8}$ hydrocarbyloxy,  $C_{1-8}$ hydrocarbyloxy substituted with one or more A,  $C_{1-8}$ heterohydrocarbyloxy,  $C_{1-8}$ heterohydrocarbyloxy substituted with one or more A, mesyl, tosyl, pentafluorophenyl, -O-succinimidyl -S-succinimidyl, or phenyloxy substituted with one or more A.

10

37. A method of any of claims 1, 2, 8-10 or 13-36 or a product of any of claims 3-7, 11, 12 or 18-36 wherein  $Ar^2$  is independently cyclopropyl, cyclopropyl substituted with one or more A, aryl, aryl substituted with one or more A, heteroaryl, or heteroaryl substituted with one or more A.

15

38. A method of any of claims 1, 2, 8-10 or 13-37 or a product of any of claims 3-7, 11, 12 or 18-37 wherein  $Ar^2$  is

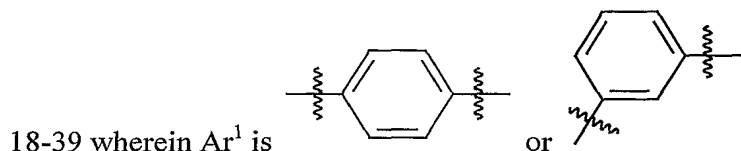


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39. A method of any of claims 1, 2, 8-10 or 13-38 or a product of any of claims 3-7, 11, 12 or 18-38 wherein  $\text{Ar}^1$  is independently cyclopropylene, cyclopropylene substituted with one or more A, arylene, arylene substituted with one or more A, heteroarylene, or heteroarylene substituted with one or more A.

5

40. A method of any of claims 1, 2, 8-10 or 13-39 or a product of any of claims 3-7, 11, 12 or



41. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein  $\text{L}^5$  is O or S.

42. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein  $\text{L}^5$  is  $-\text{E}^5-$ ,  $-(\text{D}^5)_{t'}-$ ,  $-(\text{E}^5-\text{D}^5)_{t'}-$ ,  $-(\text{D}^5-\text{E}^5)_{t'}-$ ,  $-\text{E}^5-(\text{D}^5-\text{E}^5)_{t'}-$  or  $-\text{D}^5-(\text{E}^5-\text{D}^5)_{t'}-$ ,

where:

15  $\text{D}^5$  is independently  $\text{C}_{1-8}$ hydrocarbylene or  $\text{C}_{1-8}$ hydrocarbylene substituted with one or more A;

$\text{E}^5$  is independently  $-\text{Z}^5-$ ,  $-\text{C}(=\text{Z}^5)-$ ,  $-\text{Z}^5\text{C}(=\text{Z}^5)-$ ,  $-\text{C}(=\text{Z}^5)\text{Z}^5-$ ,  $-\text{Z}^5\text{C}(=\text{Z}^5)\text{Z}^5-$ ,  $-\text{S}(=\text{O})-$ ,  $-\text{Z}^5\text{S}(=\text{O})-$ ,  $-\text{S}(=\text{O})\text{Z}^5-$ ,  $-\text{Z}^5\text{S}(=\text{O})\text{Z}^5-$ ,  $-\text{S}(=\text{O})_2-$ ,  $-\text{Z}^5\text{S}(=\text{O})_2-$ ,  $-\text{S}(=\text{O})_2\text{Z}^5-$ ,  $-\text{Z}^5\text{S}(=\text{O})_2\text{Z}^5-$ , where  $\text{Z}^5$  is independently O, S or  $\text{N}(\text{R}^5)$  and where  $\text{R}^5$  is independently H,  $\text{C}_{1-8}$ hydrocarbyl or  $\text{C}_{1-8}$ hydrocarbyl substituted with one or more A; and

$t' = 1$  or more.